

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 1 352 697 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
15.10.2003 Bulletin 2003/42

(51) Int Cl.7: **B23B 27/14**, C23C 30/00,
C23C 16/30, C23C 16/40

(21) Application number: 03005966.1

(22) Date of filing: 18.03.2003

(84) Designated Contracting States:
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IT LI LU MC NL PT RO SE SI SK TR**
Designated Extension States:
AL LT LV MK

(30) Priority: 20.03.2002 SE 0200870

(71) Applicant: **SECO TOOLS AB**
S-737 82 Fagersta (SE)

(72) Inventors:
• **Larsson, Andreas**
737 47 Fagersta (SE)
• **Sulin, Anette**
737 43 Fagersta (SE)
• **Pettersson, Lena**
737 90 Ängelsberg (SE)

(74) Representative: **Taquist, Lennart**
SECO TOOLS AB
732 82 FAGERSTA (SE)

(54) **Coated cutting tool insert**

(57) The present invention relates to a coated cemented carbide inserts (cutting tool), particularly useful for milling at high cutting speeds in steels and milling in hardened steels.

The inserts are characterised by a WC-Co cement-

ed carbide containing NbC and TaC and a W-alloyed binder phase and a coating including a first, innermost layer of $TiC_xN_yO_z$ with equiaxed grains, a layer of $TiC_xN_yO_z$ with columnar grains and at least one layer of Al_2O_3 consisting essentially of the κ -phase.

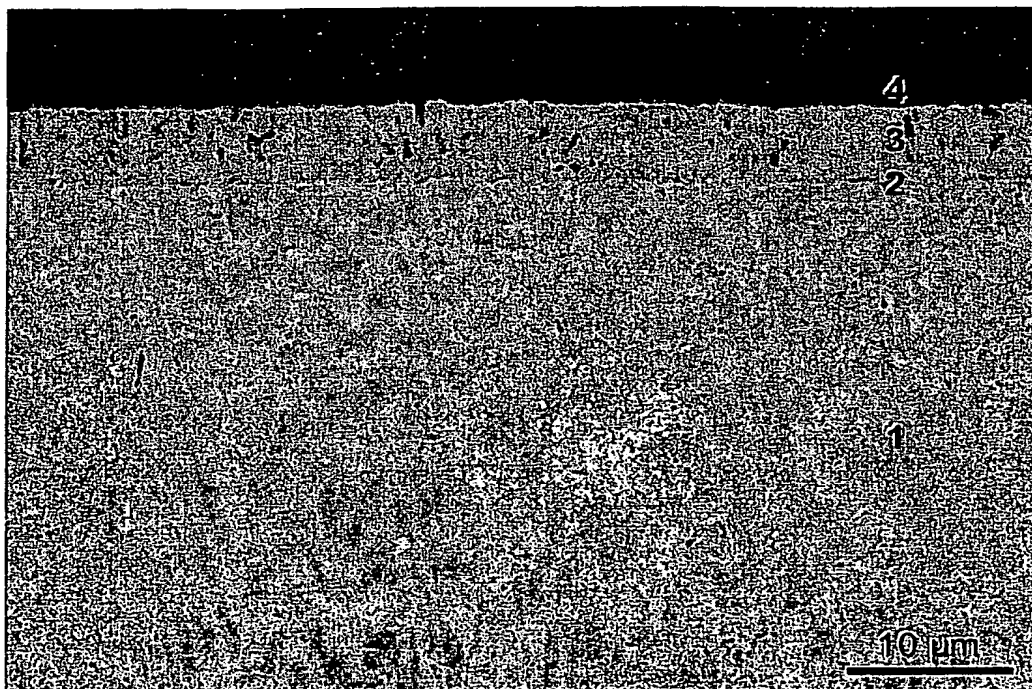


Fig 1

BEST AVAILABLE COPY

EP 1 352 697 A2

Description

[0001] The present invention relates to a coated cemented carbide insert (cutting tool), particularly useful for milling at high cutting speeds in steels and milling in hardened steels.

[0002] During machining of steels, stainless steels and cast irons with coated cemented carbide tools, the cutting edges are worn according to different wear mechanisms, such as chemical wear, abrasive wear and adhesive wear. At high cutting speeds, the amount of heat generated in the cutting zone is considerable and a plastic deformation of the cutting edge may occur, which in turn yields an enhanced wear by other mechanisms. The domination of any of the wear mechanisms is determined by the application, and is dependent on both properties of the work piece and applied cutting parameters. In milling applications, the tool life is also often limited by edge chipping caused by so-called comb cracks that form perpendicular to the cutting edge. The cracks originate from the varying thermal and mechanical loads that the cutting edge is subjected to during the intermittent cutting process. This is often even more evident in machining with coolant, which enhances the thermal variations.

[0003] Measures can be taken to improve the cutting performance with respect to a specific wear type. However, very often such actions will have a negative effect on other wear properties and successful tool composite materials must be designed as careful optimizations of numerous properties. A simple measure to increase the abrasive wear resistance and resistance to plastic deformation is to lower the binder phase content. However, this will also diminish the toughness of the cutting insert which can substantially lower the tool life in applications where factors like vibrations or the presence of casting or forging skin put demands on such properties. An alternative way to increase the deformation resistance is to add cubic carbides like TiC, TaC and/or NbC. This will also increase the wear resistance when machining at high cutting edge temperatures. However, this addition has a negative influence on comb crack formation and edge chipping tendencies.

[0004] Since it is obviously difficult to improve all tool properties simultaneously, commercial cemented carbide grades have usually been optimized with respect to one or few of the above mentioned wear types. Consequently they have also been optimized for specific application areas.

[0005] US 6,062,776 discloses a coated cutting insert particularly useful for milling of low and medium alloyed steels and stainless steels with raw surfaces such as cast skin, forged skin, hot or cold rolled skin or pre-machined surfaces under unstable conditions. The insert is characterized by a WC-Co cemented carbide with a low content of cubic carbides and a rather low W-alloyed binder phase and a coating including an innermost layer of $TiC_xN_yO_z$ with columnar grains and a top layer of TiN and an inner layer of $\kappa-Al_2O_3$.

[0006] US 6,177,178 describes a coated milling insert particularly useful for milling in low and medium alloyed steels with or without raw surface zones during wet or dry conditions. The insert is characterised by a WC-Co cemented carbide with a low content of cubic carbides and a highly W-alloyed binder phase and a coating including an inner layer of $TiC_xN_yO_z$ with columnar grains, an inner layer of $\kappa-Al_2O_3$ and, preferably, a top layer of TiN.

[0007] WO 01/16389 discloses a coated milling insert particularly useful for milling in low and medium alloyed steels with or without abrasive surface zones during dry or wet conditions at high cutting speed, and milling hardened steels at high cutting speed. The insert is characterized by WC-Co cemented carbide with a low content of cubic carbides and a highly W-alloyed binder phase and a coating including an innermost layer of $TiC_xN_yO_z$ with columnar grains and a top layer of TiN and an inner layer of $\kappa-Al_2O_3$.

[0008] EP 1103635 provides a cutting tool insert particularly useful for wet and dry milling of low and medium alloyed steels and stainless steels as well as for turning of stainless steels. The cutting tool is comprised of a cobalt cemented carbide substrate with a multi-layer refractory coating thereon. The substrate has a cobalt content of 9.0-10.9 wt% and contains 1.0-2.0 wt% TaC/NbC. The coating consists of an MTCVD $TiC_xN_yO_z$ layer and a multi-layer coating being composed of $\kappa-Al_2O_3$ and $TiC_xN_yO_z$ layers.

[0009] It has now been found that enhanced cutting performance can be obtained by combining many different features of the cutting tool. Preferably for milling, the cutting insert has excellent performance at high cutting speeds in low and medium alloyed steel as well as milling in hardened steels. At these cutting conditions, the cutting tool according to the invention displays improved properties with respect to many of the wear types mentioned earlier.

[0010] The cutting tool insert according to the present invention includes a cemented carbide substrate with a relatively low amount of cubic carbides, with a medium to highly W-alloyed binder phase and a fine to medium WC grain size. This substrate is provided with a wear resisting coating comprising an equiaxed $TiC_xN_yO_z$ layer, a columnar $TiC_xN_yO_z$ layer and at least one $\kappa-Al_2O_3$ layer.

[0011] Fig 1 shows in 2500X a coated cemented carbide substrate according to the present invention in which

1. Cemented carbide body
2. An innermost $TiC_xN_yO_z$ -layer.
3. A $TiC_xN_yO_z$ layer with columnar grains.
4. An Al_2O_3 layer consisting essentially of $\kappa-Al_2O_3$.

[0012] According to the present invention, a coated cutting tool insert is provided with a cemented carbide body having a composition of 7.9-8.6 wt% Co, preferably 8.0-8.5 wt% Co, most preferably 8.1-8.4 wt% Co; 0.5-2.1 wt%, preferably 0.7-1.8 wt%, most preferably 0.9-1.5 wt% total amount of cubic carbides of the metals Ti, Nb and Ta and balance WC. Ti, Ta and/or Nb may also be replaced by other carbides of elements from groups IVb, Vb or VIb of the periodic table. The content of Ti is preferably on a level corresponding to a technical impurity. In a preferred embodiment, the ratio between the weight concentrations of Ta and Nb is within 1.0-12.0, preferably 1.5-11.4, most preferably 3.0-10.5.

[0013] The cobalt binder phase is medium to highly alloyed with tungsten. The content of W in the binder phase may be expressed as the S-value= $\sigma/16.1$, where σ is the measured magnetic moment of the binder phase in $\mu\text{Tm}^3\text{kg}^{-1}$. The S-value depends on the content of tungsten in the binder phase and increases with a decreasing tungsten content. Thus, for pure cobalt, or a binder in a cemented carbide that is saturated with carbon, $S=1$ and for a binder phase that contains W in an amount that corresponds to the borderline to formation of η -phase, $S=0.78$.

[0014] It has now been found according to the present invention that improved cutting performance is achieved if the cemented carbide body has an S-value within the range 0.81-0.95, preferably 0.82-0.94, most preferably 0.85-0.92.

[0015] Furthermore, the mean intercept length of the tungsten carbide phase measured on a ground and polished representative cross section is in the range 0.4-0.9 μm , preferably 0.5-0.8 μm . The intercept length is measured by means of image analysis on micrographs with a magnification of 10000x and calculated as the average mean value of approximately 1000 intercept lengths.

[0016] The coating according to a preferred embodiment includes:

- a first, innermost layer of $\text{TiC}_x\text{N}_y\text{O}_z$ with $0.7 \leq x+y+z \leq 1$, preferably $z < 0.5$, more preferably $y > x$ and $z < 0.2$, most preferably $y > 0.7$, with equiaxed grains and a total thickness $< 1 \mu\text{m}$ preferably $> 0.1 \mu\text{m}$.
- a layer of $\text{TiC}_x\text{N}_y\text{O}_z$ with $0.7 \leq x+y+z \leq 1$, preferably with $z < 0.2$, $x > 0.3$ and $y > 0.2$, most preferably $x > 0.4$, with a thickness of 0.5-7 μm , preferably 1-6 μm , most preferably 2-6 μm , with columnar grains.
- at least one layer of Al_2O_3 consisting essentially of the κ -phase. The layer may also contain small amounts of the α -phase as determined by XRD-measurements. The Al_2O_3 layer has a thickness of 0.2-5 μm , preferably 0.3-4 μm , and most preferably 0.4-3 μm .
- the outermost Al_2O_3 layer can be followed by further layers ($< 1 \mu\text{m}$, preferably 0.1-0.5 μm thick) of $\text{TiC}_x\text{N}_y\text{O}_z$, $\text{HfC}_x\text{N}_y\text{O}_z$ or $\text{ZrC}_x\text{N}_y\text{O}_z$ or mixtures thereof with $0.7 \leq x+y+z \leq 1.2$, preferably with $y > x$ and $z < 0.4$, more preferably $y > 0.4$, most preferably $y > 0.7$, but an Al_2O_3 layer can also be the outermost layer.

[0017] The present invention also relates to a method of making a coated cutting tool with a composition of 7.9-8.6 wt% Co, preferably 8.0-8.5 wt% Co, most preferably 8.1-8.4 wt% Co; 0.5-2.1 wt%, preferably 0.7-1.8 wt%, most preferably 0.9-1.5 wt% total amount of cubic carbides of the metals Ti, Nb and Ta and balance WC. Ti, Ta and/or Nb may also be replaced by other carbides of elements from groups IVb, Vb or VIb of the periodic table. The content of Ti is preferably on a level corresponding to a technical impurity. In a preferred embodiment, the ratio between the weight concentrations of Ta and Nb is within 1.0-12.0, preferably 1.5-11.4, most preferably 3.0-10.5.

[0018] The desired mean intercept length depends on the grain size of the starting powders and milling and sintering conditions and has to be determined by experiments. The desired S-value depends on the starting powders and sintering conditions and also has to be determined by experiments.

[0019] The layer of $\text{TiC}_x\text{N}_y\text{O}_z$ with $0.7 \leq x+y+z \leq 1$, preferably with $z < 0.2$, $x > 0.3$ and $y > 0.2$, most preferably $x > 0.4$, having a morphology of columnar grains, is deposited with MTCVD-technique onto the cemented carbide using acetonitrile as the carbon and nitrogen source for forming the layer in the temperature range of 700-950 °C.

[0020] The innermost $\text{TiC}_x\text{N}_y\text{O}_z$ layer, the alumina layers and subsequent $\text{TiC}_x\text{N}_y\text{O}_z$, $\text{HfC}_x\text{N}_y\text{O}_z$ or $\text{ZrC}_x\text{N}_y\text{O}_z$ layers if any are deposited according to known technique.

[0021] The invention also relates to the use of cutting tool inserts according to above for dry milling at high cutting speeds in steels and dry milling in hardened steels at cutting speeds of 75-400 m/min with mean chip thickness values of 0.04-0.20 mm, depending on cutting speed and insert geometry.

Example 1.

[0022] Grade A: A cemented carbide substrate in accordance with the invention with the composition 8.2 wt% Co, 1.2 wt% TaC, 0.2 wt% NbC and balance WC, with a binder phase alloyed with W corresponding to an S-value of 0.87 was produced by conventional milling of the powders, pressing of green compacts and subsequent sintering at 1430°C. Investigation of the microstructure after sintering showed that the mean intercept length of the tungsten carbide phase was 0.65 μm . The substrate was coated in accordance with the invention with four subsequent layers deposited during the same coating cycle. The first layer was a 0.2 μm thick $\text{TiC}_x\text{N}_y\text{O}_z$ layer with $z < 0.1$ and $y > 0.6$, having equiaxed grains. The second layer was 4.1 μm of columnar $\text{TiC}_x\text{N}_y\text{O}_z$ deposited at 835-850°C with acetonitrile as carbon and nitrogen

source, yielding an approximated carbon to nitrogen ratio $x/y=1.5$ with $z<0.1$. The third layer was a $1.7\text{ }\mu\text{m}$ thick layer of Al_2O_3 deposited at approximately 1000°C and consisting essentially of the K-phase. Analysis of the Al_2O_3 layer with XRD showed minor traces of $\alpha\text{-Al}_2\text{O}_3$, but only to a level where the intensity ratio of the (012) $\alpha\text{-Al}_2\text{O}_3$ and the (022) $\kappa\text{-Al}_2\text{O}_3$ reflections were less than 1/3. Finally a layer of equiaxed nitrogen rich $\text{TiC}_x\text{N}_y\text{O}_z$ with $z<0.1$ and $y>0.8$ was deposited to a thickness of $0.2\text{ }\mu\text{m}$.

[0023] Grade B: A substrate according to grade A (according to the invention) was coated with a multilayer coating with seven layers consisting of $\text{TiC}_x\text{N}_y\text{O}_z$ ($z<0.1$). All layers were deposited using conventional CVD at 1010°C with methane and nitrogen gas as carbon and nitrogen sources. The grain morphology of each layer showed equiaxed features. The first layer was $3.1\text{ }\mu\text{m}$ of $\text{TiC}_x\text{N}_y\text{O}_z$ with a composition close to $x/y=1.6$. The thickness of each of the following six layers was $0.8\text{ }\mu\text{m}$, and the composition alternated between estimated x/y ratios of 4 and 0.25, respectively.

[0024] Grade C: A substrate with composition 7.1 wt% Co, 0.5 wt% TaC, 0.1 wt% NbC and balance WC, a binder phase alloyed with W corresponding to an S-value of 0.94, and a mean intercept length of WC in the sintered body of $1.1\text{ }\mu\text{m}$ was combined with a coating according to Grade A (according to the invention).

Operation	Face milling
Cutter diameter	125 mm
Work piece	Bar, 600 mm x 75 mm
Material	SS1672, 185 HB
Insert type	SEKN1203
Cutting speed	300 m/min
Feed	0.25 mm/tooth
Number of teeth	1
Depth of cut	2.5 mm
Width of cut	75mm.
Coolant	Yes

Results	Tool life (min)
Grade A (grade according to invention)	14
Grade B (substrate according to invention)	10
Grade C (coating according to invention)	8

[0025] The tool life was limited due to destruction of the cutting edge as consequence of the propagation of thermal cracks. This test shows that the combination of the substrate and coating according to the invention exhibits longer tool life than the same substrate in combination with prior art coating or the coating in the invention combined with a prior art substrate.

Example 2:

[0026] Grade D: A commercial cemented carbide cutting insert from a competitor with the composition 8.8 wt% Co, 1.8 wt% TaC, 0.3 wt% NbC, 0.3 wt% TiC and balance WC. The binder phase is alloyed with W corresponding to an S-value of 0.90, and the mean intercept length of the WC is $0.9\text{ }\mu\text{m}$. The insert is coated with $2.5\text{ }\mu\text{m}$ of $\text{TiC}_x\text{N}_y\text{O}_z$, $1.5\text{ }\mu\text{m}$ of Al_2O_3 and $0.4\text{ }\mu\text{m}$ of $\text{TiC}_x\text{N}_y\text{O}_z$.

Operation	Face milling
Cutter diameter	125 mm
Work piece	Bar, 600 mm x 26 mm
Material	SS2541, 240 HB
Insert type	SEKN1203

EP 1 352 697 A2

(continued)

Operation	Face milling
Cutting speed	200 m/min
Feed	0.2 mm/tooth
Number of teeth	1
Depth of cut	2.5 mm
Width of cut	26 mm
Coolant	Yes

Results	Tool life (min)
Grade A (grade according to invention)	20
Grade C (substrate according to invention)	12
Grade D (prior art)	17

[0027] The tool life was limited due to destruction of the cutting edge as consequence of propagation of comb cracks due to varying thermal and mechanical loads. In this test the coatings of the compared grades were of similar type and the differences in tool life is principally a consequence of constitutional differences between the tested substrates. The test shows that the cemented carbide substrate according to the invention exhibits longer tool life than the two grades containing less and more binder phase.

Example 3:

[0028] Grade E: A commercial cemented carbide cutting insert with composition 9.4 wt% Co, 7.2 wt% TaC, 0.1 wt% NbC, 3.4 wt% TiC and balance WC. The binder phase is alloyed with W corresponding to an S-value of 0.85, and the mean intercept length of the WC is 0.7 μ m. The insert is coated with a 1.5 μ m thick $Ti_xAl_{1-x}N$ layer.

Operation	Copy milling
Cutter diameter	35 mm
Work piece	Bar, 350 mm x 270 mm
Material	SS2242, 38 HRC
Insert type	RPHT1204
Cutting speed	200 m/min
Feed	0.22 mm/tooth
Number of teeth	3
Depth of cut	2 mm
Width of cut	5-32 mm
Coolant	No

Results	Tool life (min)
Grade A (grade according to invention)	65
Grade B (substrate according to invention)	25
Grade E (prior art)	41

[0029] The tool life was limited by flank wear and edge chipping. This test shows that compared to straight $TiC_xN_yO_z$

based coatings, the coating according to the invention gives better protection against abrasive wear and cracking due to thermal loads. The shorter tool life of Grade E shows the negative effect of high cubic carbide content on cutting edge strength and edge chipping resistance.

Example 4:

[0030]

Operation	Face milling
Cutter diameter	125 mm
Work piece	Bar, 300 mm x 80 mm
Material	SS2244, 48 HRC
Insert type	SEKN1203
Cutting speed	200 m/min
Feed	0.15 mm/tooth
Number of teeth	1
Depth of cut	2.5 mm
Width of cut	40 mm
Coolant	No

Results	Tool life (min)
Grade A (grade according to invention)	15
Grade C (coating according to invention)	7

[0031] In this test, the tool life is limited by edge chipping and cracking leading to rupture of the cutting edge. The differences in tool life show the effect of a smaller grain size in combination with a slightly higher Co content. These measures give a somewhat better plastic deformation resistance of the cutting edge with maintained toughness properties.

Claims

1. A cutting tool insert, comprising a cemented carbide body and a coating particularly useful in milling at high cutting speeds in low and medium alloyed steels and milling in hardened steels **characterized in** a composition of said body of 7.9-8.6 wt%, preferably 8.0-8.5 wt% Co, 0.5-2.1 wt%, preferably 0.7-1.8 wt% a total amount of cubic carbides of the metals Ta and Nb, the ratio between the weight concentrations of Ta and Nb is within 1.0-12.0, preferably 1.5-11.4 and balance WC with a mean intercept length in the range 0.4-0.9 μm , preferably 0.5-0.8 μm and the binder phase being alloyed with W corresponding to an S-value within the range 0.81-0.95, preferably 0.82-0.94 and **in that** said coating comprises
 - a first, innermost layer of $\text{TiC}_x\text{N}_y\text{O}_z$ with $0.7 \leq x+y+z \leq 1$, preferably $z < 0.5$, more preferably $y > x$ and $z < 0.2$, with equiaxed grains and a total thickness $< 1 \mu\text{m}$, preferably $> 0.1 \mu\text{m}$
 - a layer of $\text{TiC}_x\text{N}_y\text{O}_z$ with $0.7 \leq x+y+z \leq 1$, preferably with $z < 0.2$ $x > 0.3$ and $y > 0.2$, preferably $x > 0.4$, with a thickness of 0.5-7 μm , preferably 1-6 μm , with columnar grains
 - at least one layer of Al_2O_3 consisting essentially of the K-phase possibly containing small amounts of the α -phase as determined by XRD-measurements and having a thickness of 0.2-5 μm , preferably 0.3-4 μm .
2. A cutting tool insert according to the preceding claim **characterized in** furthermore comprising an outer layer of $\text{TiC}_x\text{N}_y\text{O}_z$, $\text{HfC}_x\text{N}_y\text{O}_z$ or $\text{ZrC}_x\text{N}_y\text{O}_z$ or mixtures thereof with $0.7 \leq x+y+z \leq 1.2$ preferably with $y > x$ and $z < 0.4$, more preferably $y > 0.4$.

3. A method of making a cutting tool insert, comprising a cemented carbide body and a coating particularly useful in milling at high cutting speeds in low and medium alloyed steels and milling in hardened steels **characterized in** depositing on a cemented carbide body with a composition of 7.9-8.6 wt%, preferably 8.0-8.5 wt% Co, 0.5-2.1 wt%, preferably 0.7-1.8 wt% a total amount of cubic carbides of the metals Ta and Nb, the ratio between the weight concentrations of Ta and Nb is within 1.0-12.0, preferably 1.5-11.4 and balance WC with a mean intercept length in the range 0.4-0.9 μm , preferably 0.5-0.8 μm and the binder phase being alloyed with W corresponding to an S-value within the range 0.81-0.95, preferably 0.82-0.94 a coating comprising
- a first, innermost layer of $\text{TiC}_x\text{N}_y\text{O}_z$ with $0.7 \leq x+y+z \leq 1$, preferably $z < 0.5$, more preferably $y > x$ and $z < 0.2$, with equiaxed grains and a total thickness $< 1 \mu\text{m}$, preferably $> 0.1 \mu\text{m}$
 - a layer of $\text{TiC}_x\text{N}_y\text{O}_z$ with $0.7 \leq x+y+z \leq 1$, preferably with $z < 0.2$, $x > 0.3$ and $y > 0.2$, preferably $x > 0.4$, with a thickness of 0.5-7 μm , preferably 1-6 μm , with columnar grains
 - at least one layer of Al_2O_3 consisting essentially of the κ -phase possibly containing small amounts of the α -phase as determined by XRD-measurements and having a thickness of 0.2-5 μm , preferably 0.3-4 μm .
4. The method of claim 3 **characterized in** depositing an outer layer of $\text{TiC}_x\text{N}_y\text{O}_z$, $\text{HfC}_x\text{N}_y\text{O}_z$ or $\text{ZrC}_x\text{N}_y\text{O}_z$ or mixtures thereof with $0.7 \leq x+y+z \leq 1.2$, preferably with $y > x$ and $z < 0.4$, more preferably $y > 0.4$.
5. Use of a cutting tool insert according to claims 1-4 for dry milling at high cutting speeds in steels and dry milling in hardened steels at cutting speeds of 75-400 m/min at mean chip thickness values of 0.04-0.2 mm, depending on cutting speed and insert geometry.

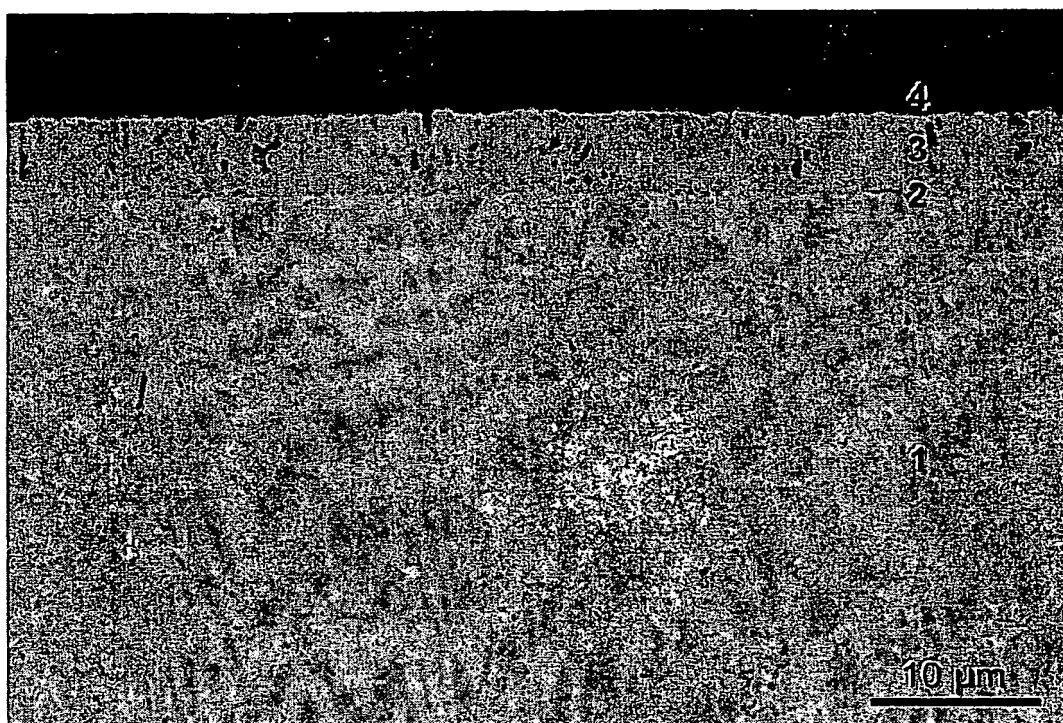
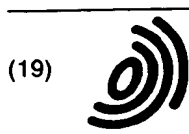


Fig 1



(19)

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 1 352 697 A3

(12)

EUROPEAN PATENT APPLICATION

(88) Date of publication A3:
06.05.2004 Bulletin 2004/19

(51) Int Cl.7: **B23B 27/14**, C23C 30/00,
C23C 16/30, C23C 16/40

(43) Date of publication A2:
15.10.2003 Bulletin 2003/42

(21) Application number: **03005966.1**

(22) Date of filing: **18.03.2003**

(84) Designated Contracting States:
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IT LI LU MC NL PT RO SE SI SK TR**
Designated Extension States:
AL LT LV MK

(30) Priority: **20.03.2002 SE 0200870**

(71) Applicant: **SECO TOOLS AB**
S-737 82 Fagersta (SE)

(72) Inventors:
• **Larsson, Andreas**
737 47 Fagersta (SE)
• **Sulin, Anette**
737 43 Fagersta (SE)
• **Pettersson, Lena**
737 90 Ängelsberg (SE)

(74) Representative: **Taquist, Lennart**
SECO TOOLS AB
732 82 FAGERSTA (SE)

(54) **Coated cutting tool insert**

(57) The present invention relates to a coated cemented carbide inserts (cutting tool), particularly useful for milling at high cutting speeds in steels and milling in hardened steels.

The inserts are characterised by a WC-Co cement-

ed carbide containing NbC and TaC and a W-alloyed binder phase and a coating including a first, innermost layer of $\text{TiC}_x\text{N}_y\text{O}_z$ with equiaxed grains, a layer of $\text{TiC}_x\text{N}_y\text{O}_z$ with columnar grains and at least one layer of Al_2O_3 consisting essentially of the κ -phase.

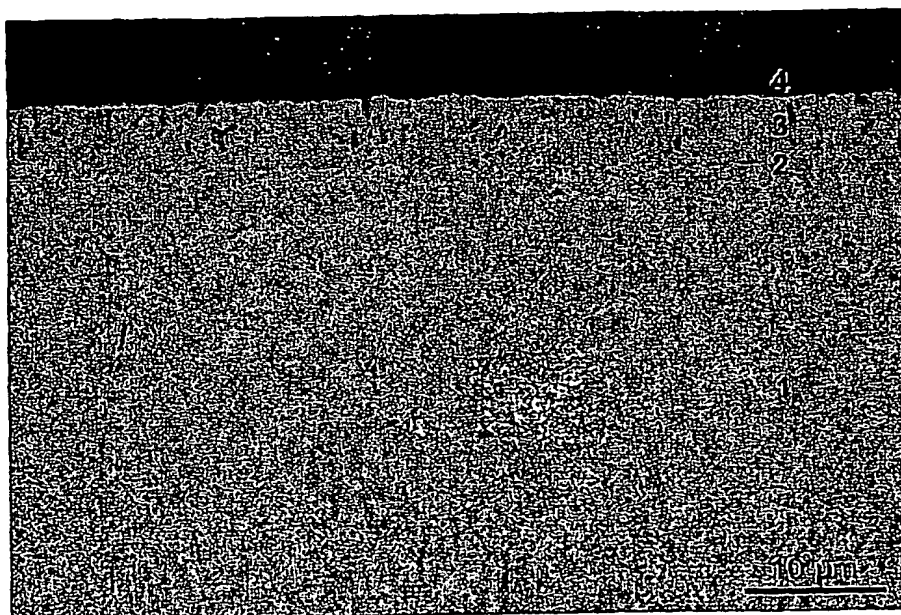


Fig 1

EP 1 352 697 A3



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 03 00 5966

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X, P	US 6 406 224 B1 (OESTLUND AAKE ET AL) 18 June 2002 (2002-06-18) * the whole document *	1-5	B23B27/14 C23C30/00 C23C16/30 C23C16/40
X	EP 1 103 635 A (SANDVIK AB) 30 May 2001 (2001-05-30) * the whole document *	1-5	
X	US 6 177 178 B1 (OSTLUND AAKE ET AL) 23 January 2001 (2001-01-23) * the whole document *	1-5	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			C23C B23B
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 16 March 2004	Examiner Harbron, J
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

EPO FORM 1503 (03.02) (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 03 00 5966

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

16-03-2004

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
US 6406224	B1	18-06-2002	EP	1218558 A1		03-07-2002
			JP	2003508632 T		04-03-2003
			WO	0116389 A1		08-03-2001

EP 1103635	A	30-05-2001	SE	519903 C2		22-04-2003
			SE	519896 C2		22-04-2003
			EP	1103635 A2		30-05-2001
			JP	2001205505 A		31-07-2001
			SE	9904274 A		26-05-2001
			US	6632514 B1		14-10-2003
			SE	0000667 A		30-08-2001

US 6177178	B1	23-01-2001	AT	231565 T		15-02-2003
			AT	213283 T		15-02-2002
			AT	213282 T		15-02-2002
			BR	9611780 A		23-02-1999
			BR	9611781 A		23-02-1999
			BR	9611788 A		13-07-1999
			CN	1203636 A		30-12-1998
			CN	1203637 A		30-12-1998
			CN	1203638 A		30-12-1998
			DE	69619272 D1		21-03-2002
			DE	69619272 T2		31-10-2002
			DE	69619275 D1		21-03-2002
			DE	69625934 D1		27-02-2003
			DE	69625934 T2		13-11-2003
			EP	0871796 A1		21-10-1998
			EP	0874919 A1		04-11-1998
			EP	0870073 A1		14-10-1998
			IL	124474 A		26-08-2001
			IL	124475 A		26-08-2001
			IL	124476 A		26-08-2001
			JP	2000515587 T		21-11-2000
			JP	2000515588 T		21-11-2000
			JP	2000515433 T		21-11-2000
			WO	9720081 A1		05-06-1997
			WO	9720082 A1		05-06-1997
			WO	9720083 A1		05-06-1997
			US	6062776 A		16-05-2000
			US	6200671 B1		13-03-2001

EPO FORM P0458

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

THIS PAGE BLANK (USPTO)

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)